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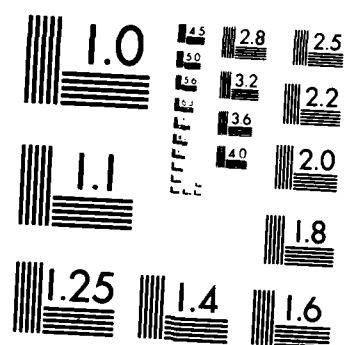
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Reactions of the heteroborane, 6-thia-nido-decaborane(11), have been examined under a variety of conditions with the specific objective of determining the ability of this compound to hydroborate alkenes and alkynes. Under room temperature conditions, reaction with alkenes occurred exclusively at position 9 of the thiaborane cage. Steric factors influence the course of the reaction with respect to the organic moiety, and evidence is cited

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as to the reaction's reversibility.

At higher temperatures, additional alkyl groups could be attached to the thiaborane cage as a consequence of multiple hydroboration steps. The results are consistent with a mechanism in which hydroboration occurs only at position 9 of the cage followed by isomerization caused by the fluxional nature of the heteroborane cage.

It was found that thiaborane will hydroborate polybutadiene and can act as a cross linking agent.

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A STUDY OF THE REACTIONS OF 6-THIA-NIDO-DECABORANE(11)

by

Robert C. Taylor and Neil M. Canter

Department of Chemistry
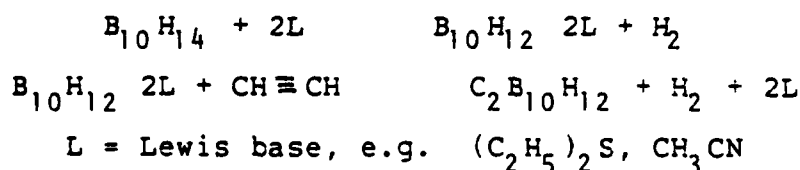The University of Michigan
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January 3, 1983

A Study Of Hydroboration Reactions Of 6-Thia-Nido-Decaborane(11)

Initial studies of the hydroboration reactivity of 6-thia-nido-decaborane(11) (6-SB_9H_{11}) were carried out by Rudolph and Meneghelli in 1978 who showed [1] that this compound added to olefins and alkynes to form monoorganothiaboranes. Spectral analysis established that the exo B-H group located at position nine of the thiaborane cage was the site of the reaction. Olefins adding to the polyhedral thiaborane cage did so in a regiospecific, anti-Markovnikov orientation [2]. However, 6-SB_9H_{11} did not react with alkynes to give dicarbathiaborane species in analogy to the isoelectronic nido-$B_{10}H_{14}$ which yields carboranes upon treatment with alkynes , as illustrated below [3]:

$$B_{10}H_{14} + 2L \qquad B_{10}H_{12} \cdot 2L + H_2$$

$$B_{10}H_{12} \cdot 2L + CH \equiv CH \qquad C_2B_{10}H_{12} + H_2 + 2L$$

$$L = \text{Lewis base, e.g. } (C_2H_5)_2S, \; CH_3CN$$

The present work was initiated to explore the hydroboration reactions of 6-SB_9H_{11} further to determine if the compound displayed any unusual characteristics not possessed by more conventional hydroboration reagents, and to see if boron atoms at other than position nine could be involved in the reaction. In the case of other (non-cage) alkylboranes, Brown has found [4,5] that isomerization and displacement occur at elevated temperatures suggesting a reversible hydroboration reaction involving carbon-boron bond breakage followed by reattachment. If similar processes occur in the case of

monoalkylthiaborane cages, then an alkyl group initially attached at position nine might migrate to another position on the cage.

Experimental Results

The following section presents a review and summary of experimental results obtained in the investigation of the hydroboration reactions between 6-thia-nido-decaborane(11) and various alkenes and alkynes. Conditions under which reactions occurred are stated but specific details such as starting amounts, yields, etc., for the most part have been omitted. Initial work was carried out at room temperature to explore the range and nature of hydroboration reactions of olefins. Subsequently, increasingly harsh conditions were employed to study further ramifications, particularly possible isomerizations and attachment of multiple alkyl groups onto the thiaborane cage.

All room temperature reactions were carried out for four hours in toluene, for the most part using equimolar amounts of olefin and 6-SB H . In all cases, the hydroboration involved only the boron at cage position nine with the yields showing an improvement over those reported by Rudolph and Meneghelli [1]. In the case of the asymmetric olefins styrene and cis-2-pentene, it was found that $6-SB_9H_{11}$ preferred to add to the least hindered carbon atom. In the sytrene reaction, no evidence was found for hydroboration of the carbon directly attached to the phenyl ring. Both vinyl carbons of cis-2-pentene formed bonds

with $6\text{-SB}_9\text{H}_{11}$ but the results of alkaline peroxide oxidation showed that carbon(2) was favored by a 4:1 ratio.

Further insight into room temperature hydroboration was obtained by using both cis- and trans-3-methyl-3-hexene. As anticipated, the thiaborane cage added to the least substituted carbon atom of the olefin in both cases. However, in contrast to the other olefin reactions investigated, a small amount of the reactant $6\text{-SB}_9\text{H}_{11}$ was found in the product mixture. Upon alkaline peroxide oxidation, the expected alcohol, 4-methyl-3-hexanol, was isolated. The interesting observation, however, was that a trace amount of trans-3-methyl-3-hexene was found irrespective of whether the starting material was the cis or trans compound.

An equimolar mixture of two olefins was treated with one equivalent of 6-SB H to determine the selectivity of the hydroboration agent. The terminal olefin, 1-hexene, was chosen as a standard. In reactions using cis-3-hexene and cis-3-methyl-3-hexene, the thiaborane preferred the internal olefin over 1-hexene by a 3:1 margin. However, in the case of trans-3-hexene, the ratio to 1-hexene was reduced to 1:1.

The reactivity of alkynes with $6\text{-SB}_9\text{H}_{11}$ at room temperature was studied using 1-hexyne. In this reaction, thiaborane added to carbon(1) in a syn manner to yield a hexenylthiaborane. Since the relative reactivity of alkenes versus alkynes was of interest, two types of experiments were then performed. In one the preference of the reacting thiaborane for a double or triple bond in the same molecule was examined by the reaction with

hex-1-ene-5-yne. The results indicated that $6-SB_9H_{11}$ showed no preference for either site. Although GC/MS could not separate the products, boron-11 and carbon-13 NMR clearly showed that $6-SB_9H_{11}$ reacted with both functionalities and that the two products were present in nearly equal amounts. In the second experiment, the preference of $6-SB_9H_{11}$ for a double versus a triple bond when the two were in separate molecules was examined by a competition reaction between 1-henene and 1-hexyne under conditions described previously. In this case, GC/MS analysis revealed that the thiaborane perfered the olefin over the alkyne by a ratio of 3:2. This ratio was not altered when a large excess (20 fold) of both substances was used.

At higher temperatures, as might be anticipated, the chemistry of 6-thia-nido-decaborane(11) grows considerably more complex. As a beginning, monoalkylthiaboranes were subjected to progressively higher temperatures to test their thermal stability and to explore their proclivity towards rearrangement. Refluxing in benzene (80°C), toluene (110°C) and meta-xylene (136°C) resulted in no reaction. However, the use of mesitylene (164°C) and tetralin (207°C) led to the formation of dialkylthiaboranes and trialkylthiaboranes. As a specific example, after refluxing cis-2-pentene and $6-SB_9H_{11}$ for five days in mesitylene, fractional sublimation of the product mixture yielded $1,9-(dipentyl)-6-SB_9H_{10}$. The presence of the second pentyl group was clearly indicated by boron-11 NMR data but the presence of aryl coupling side products complicated the separation. Treatment of $6-SB_9H_{11}$ with cis-3-hexene in

refluxing tetralin for 26 hours produced a mixture containing 1,9-(dihexyl)-6-SB_9H_9 and 1,3,9-(trihexyl)-6-SB_9H_8. After separation by fractional sublimation, subsequent alkaline peroxide oxidation of the fraction containing over 90% of 1,9-(dihexyl)-6-SB_9H_9 yielded 3-hexanol, 2-hexanol and 1-hexanol in the ratio 38:56:6.

As a result of problems with reproducibility, the method of carrying out the reaction was changed at this point. Instead of refluxing the reaction mixture, the reactants (including solvent when desired) were sealed in a glass tube under vacuum and then heated in a temperature controlled furnace. To explore the multiple hydroboration reaction under these conditions, the mono-alkyl species, 9-(3'-hexyl)-6-SB_9H_{10}, and a ten-fold excess of cis-3-hexene were heated at several temperatures for varying times. The results are listed in Table 1.

Table 1

Effect of Time and Temperature on the Alkylation of 6-SB_9H_{11}

			Product Composition		
Yield	Temp.	Time	Monohexyl	Dihexyl	Trihexyl
88 %	165 C	2 days	77.2%	21.5%	1.3%
62.9%	180	2 days	65.3%	34.7%	-
87.3%	180	3 days	61.0%	36.0%	3.0%
91.1%	190	2 days	50.5%	45.1%	4.4%
83.6%	190	3 days	11.8%	59.2%	29.0%

The overall course of the reaction is depicted below.
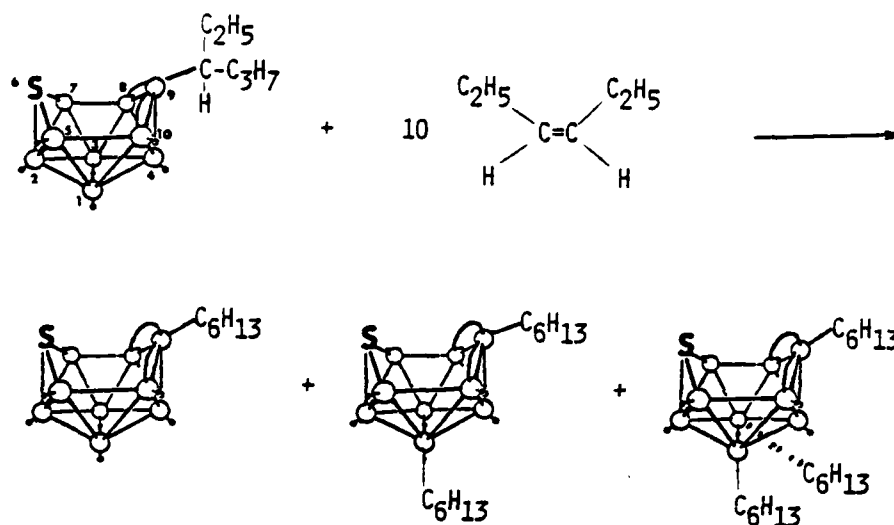
Preparative gas chromatography was used to isolate the dihexyl species and boron-11 NMR spectroscopy was used to establish the substitution positions of the various alkylated compounds.

Investigation of the multiple addition reaction was extended by utilizing other olefins. In particular, sealed tube reactions were carried out at 200°C using the monoalkylthiaborane and a ten-fold excess of the corresponding substrate dissolved in tetraline. Alkenes investigated in this way included cis-3-hexene, cis-2-pentene, 1-octene and trans-4-octene. In the product mixtures, at least 83% of the alkylthiaboranes isolated were trialkyl species, the remainder being dialkyl. Some side products attributed to involvement of the tetralin were also seen. Alkaline peroxide oxidation of the

trialkyl species resulted in a mixture of alcohols. For example, the trihexyl species prepared from cis-3-hexene yielded 3-hexanol, 2-hexanol and 1-hexanol in the ratio 36:61;3, a result not markedly different from that found from the oxidation of the dihexyl species mentioned previously. The trisubstituted material was made up of a number of carbon chain isomers for which it was impractical to attempt a separation. The products of the 1-octene reaction consisted almost entirely of carbon chains with boron moieties attached at the terminal position. only 5% being attached at carbon(2). This is further evidence that the terminal carbon of a chain is a preferred position in agreement with previous observations by Brown on organoboranes [4]. The conditions used in these reactions, namely, sealed tubes with or without solvent heated at 200 C with excess olefin yielded only trace amounts of the tetralkyl species. When a sealed tube reaction was carried out in the absence of the moderating influence of the tetralin solvent, di- and trialkyl- species in both the closo and nido forms were produced. The amount of closo compounds appeared related to the location of the double bond in the olefin, the largest amounts resulting from the use of terminal olefins in which case the percentage was significant.

A number of pyrolysis experiments were carried out to shed additional light on the isomerization processes. Monoalkylthiaboranes when heated for twelve hours in a sealed tube at 200°C gave a 20 to 25% conversion to dialkylthiaboranes. In addition, small amounts of closo-1-SB_9H_9 [6],

closo-1-$SB_{11}H_{11}$ [7] and (alkyl)-1-$SB_{11}H_{10}$ were detected by GC/MS. Oxidation of the pyrolysis product mixtures led to a variety of isomeric alcohols reflecting isomerization of the carbon moiety. When the substrate was cis-3-hexene, 3-hexanol, 2-hexanol and 1-hexanol were found in a ratio of 45:52:3. With 9-(1'-octyl)-6-SB_9H_{10}, although 1-octanol comprised 75% of the oxidation mixture, measureable amounts of 2-octanol, 3-octanol and 4-octanol were found by GC/MS indicating that, while driving force favoring attachment of the cage to the terminal atom of the carbon chain is significant, it is not overwhelming in magnitude.

The reactions of alkylthiaboranes described up to now have involved homogeneous compounds, i.e. compounds in which all alkyl groups on the thiaborane cage were identical. To delineate the nature of high temperature hydroboration more fully, heterogeneous olefin reactions were investigated from the point of view of displacement processes. In a specific experiment, for example, treatment of 9-(1'-octyl)-6-SB_9H_{10} with ten equivalents of cis-3-hexene resulted in a mixture of mono-, di- and trialkylthiaboranes with virtually all of the possible combinations of hexyl and octyl groups being identified in the product compounds. The statistically favored combinations, 1,9-(hexyloctyl)-6-SB_9H_9 and 1,3,9-(dihexyloctyl)-6-SB_9H_8, predominated. However, the detection of 1,9-(dihexyl)-SB_9H_9 and 1,3,9-(trihexyl)-SB_9H_8 established that the octyl side chain originally on the cage was displaced during the reaction. When trihexylthiaborane starting material reacted with an excess of

1-octene, displacement again occurred. The products remained
exclusively trialkyl and included both the mono- and dioctyl
species.

It was mentioned above that at 200°C hydroboration stopped
at the trialkyl stage although six unsubstituted borons remained
in the thiaborane cage. More stringent conditions were employed
in a few experiments to see if additional substitution could be
achieved. Some success in this respect was achieved by heating
reaction mixtures containing excess olefin for three days at
240 C. In addition to trialkly species, GC/MS analysis
identified both tetra- and pentasubstituted thiaboranes in
measureable amounts. However, a substantial amount of cage
closure occurred and, presumably, all three type of substitution
products were present in both nido and closo forms.
Unfortunately, too great a variety of isomeric products resulted
to allow the fourth and fifth hydroboration sites to be
assigned.

The reactions of 6-thia-nido-decaborane(11) with alkynes
above room temperature were examined in a fashion similar to
that used for olefins. Under the relatively mild conditions of
refluxing toluene, terminal alkynes could be dihydroborated by
6-thia-nido-decaborane(11) to give a classical dihydroboration
product analogous to that produced by non-cage boranes [8].
NMR spectral data clearly indicated that two thiaborane cages
were bonded to the terminal carbon atom. That the hydroboration
proceeded stepwise was shown by the fact that refluxing
$9-(1'-hex-1'-enyl)-6-SB_9H_{10}$ with $6-SB_9H_{11}$ resulted in the

expected dihydroborated product. When the triple bond was located in the center of a carbon chain, harsher conditions were required to cause reaction. With 3-hexyne, the monohydroborated product could be formed fairly easily but further reaction did not occur until the initial product was heated in a sealed tube at 190°C. The final, rather complex, product mixture consisted principally of several monohexylthiaboranes and monohexenylthiaboranes together with minor amounts of dihexyl- and dihexenylthiaboranes plus dihydroborated species. Alkaline peroxide oxidation yielded 2-hexanol, 3-hexanol, 2-hexanone and 3-hexanone. A number of different reactions appeared to have taken place under the conditions described. The presence of monohexylthiaboranes resulted from the hydrogenation of the double bond in some unknown fashion without accompanying cage closure. Both $9-(3'-hex-3'-enyl)-6-SB_9H_{10}$ and $9-(3'-hexyl)-6-SB_9H_{10}$ appeared to have undergone thermal isomerization while the presence of a double bond in the monohexenylthiaborane species enabled a further reaction to occur to yield dihydroboration products. Moreover, since cage rearrangement is facile at the temperatures used, the opportunity exists for multiple hydroboration reactions to occur leading to a dialkyl or dialkenyl species. With the conditions described, on a trace amount of cage closure was detected with boron-11 NMR.

A few experiments were carried out which showed that $6-SB_9H_{11}$ would add to polybutadiene at room temperature. Subsequent heating of the product at 165° C for four hours

resulted in a crosslinked polymer, presumably tying together two chains by attachment through the boron(1) and boron(9) positions of the cage. In the absence of the thiaborane, polybutadiene did not crosslink under comparable conditions. The possible polymer reaction sequence is depicted below.
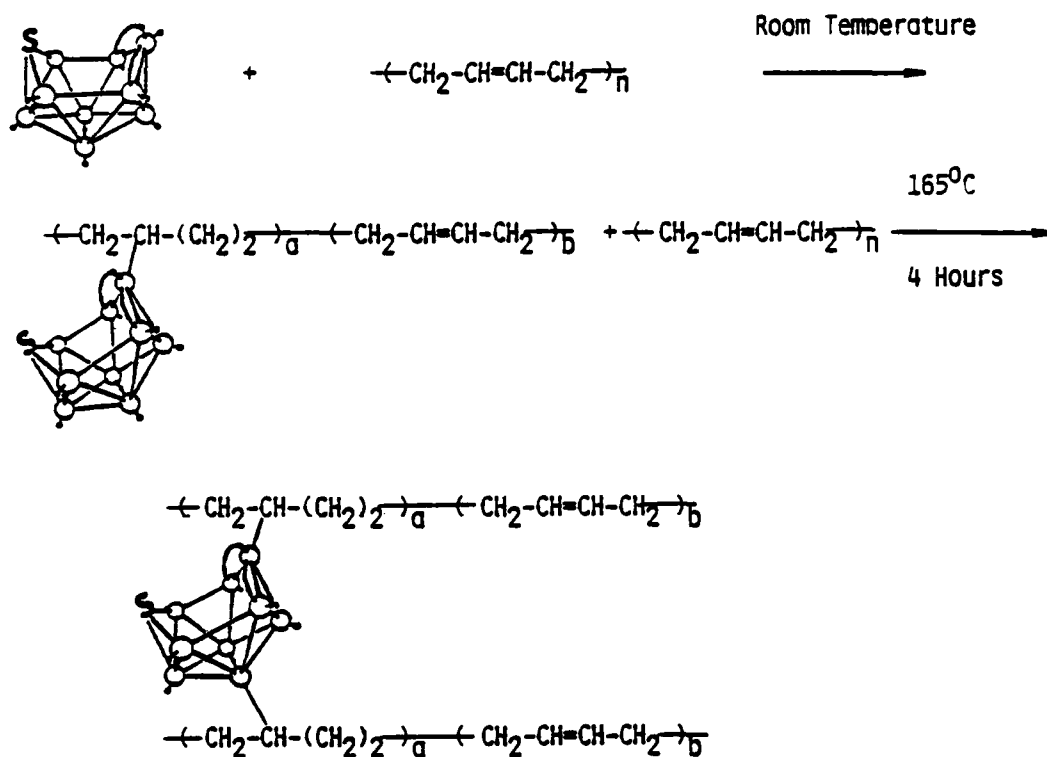
Discussion

The complete absence of di- and trialkyl thiaboranes among the products of room temperature reactions strongly suggests that the principal, if not the only, reaction site involved in hydroboration reactions by 6-thia-nido-decaborane(11) is position 9, located directly across the open face of the cage

from the sulfur atom. In the hydroboration of asymmetric compounds, the bulky nature of the thiaborane clearly is a factor in directing attachment of the boron moiety onto the least substituted carbon atom of the multiple bond. In most cases, it was found that the reaction proceeded to completion leaving no detectable amounts of reactants. The exceptions occurred in the case of hindered olefins. For example, when either cis or trans 3-methyl-3-hexenes were reacted, small amounts of starting material were found in the final mixture. The equilibrium position therefore appears dependent upon steric factors. A more significant finding when cis-3-methyl-3-hexene was hydroborated was the identification of a small amount of trans-3-methyl-3-hexene and its derived alcohol (4-methyl-3-hexanol) in the mixture resulting from alkaline peroxide oxidation products. There was no detectable amount of the cis isomer remaining. The most plausible mechanism by which to explain the cis to trans conversion involves the reaction of 6-SB H with the olefin to produce an alkylthiaborane complex. This complex may either be an unstable species in equilibrium with the reactants, or an intermediate analogous to the four-centered transition state proposed by Brown for reactions of non-cage organoboranes [9]. In either case, the nature of the adduct species must be such that the olefin, upon regeneration, can assume the thermodynamically most favored form. A schematic depiction of the reaction steps follows.
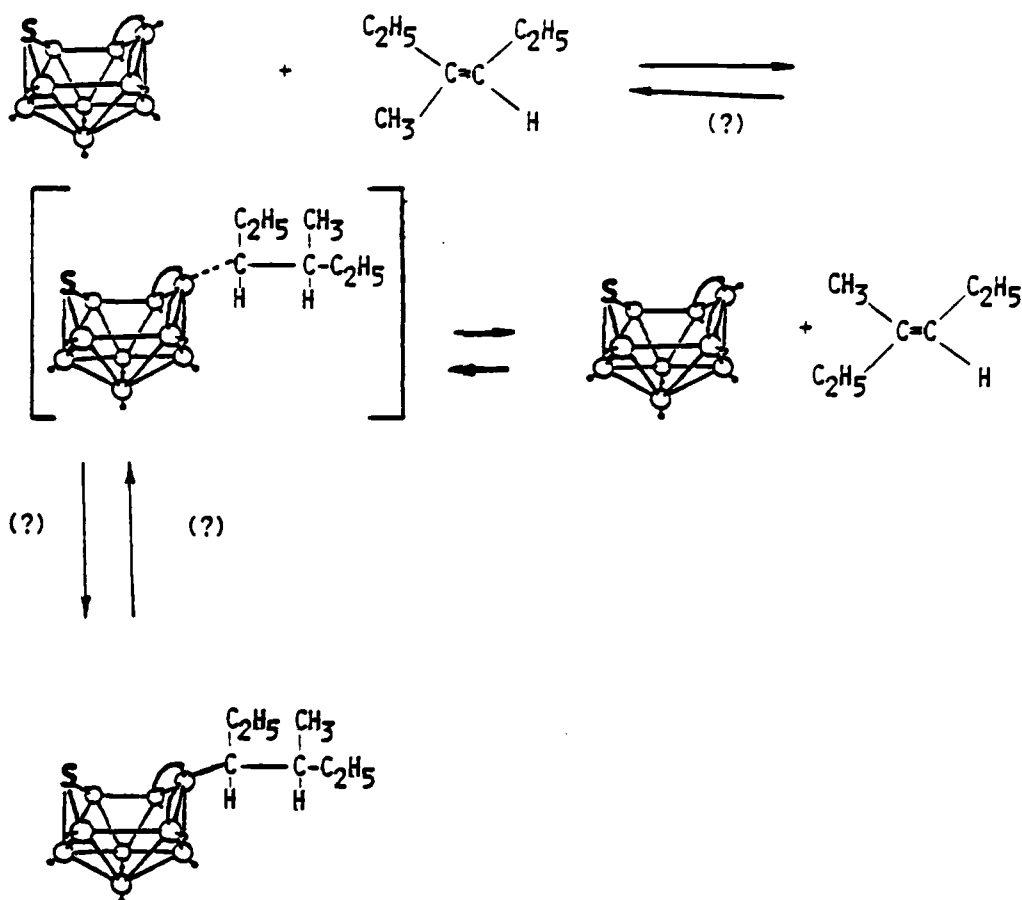
That the course of the reaction is not controlled solely by steric factors is shown by the competition reactions in which 1-hexene was used as a reference. Despite the reduced accessibility of a double bond in the central portion of a carbon chain, the thiaborane reacted preferentially at this position, the attraction presumably being the higher electron density associated with the internal double bond. An interesting aspect of this finding is that the behavior of thiaborane is quite different from that of non-cage alkyl

boranes [10]. Brown, for example, observed that disiamylborane reacted faster with 1-hexene than with cis-3-hexene by a factor of 50. When trans-3-hexene was used instead of the cis-3-hexene, the rate of addition of the disiamylborane to the alkene increased to approximataely 500 times the 1-hexene rate. This tendency of the thiaborane to react preferentially with sites having a high electron density in competitive situations, and the different behavior from non-cage boranes, may have some practical utility for selective hydroboration in synthetic work.

The reversible nature of the hydroboration reaction established by the experiments at room temperature, together with the knowledge that the thiaborane cage itself is fluxional, provides an adequate basis for understanding the more complex results found at higher temperatures. The reversible interconversion between the hydroborated and olefinic structures undoubtably facilitates isomerization of the carbon chain in the organic moiety. That the actual mechanism may be relatively complex, however, is shown by the fact that the point of attachment of the thiaborane cage in the hydroborated compounds tends to migrate along the carbon chain towards the end atom. Brown has also reported that non-cage alkyl boranes act in the same manner.

The production of multiply alkylated thiaborane compounds at the higher temperatures is most easily understood in terms of the well known tendency of polyhedral boron structures to rearrange and scramble the borons among the cage positions [11]. As a result, a carbon chain originally attached at position 9

following a hydroboration step can end up at position 1 or 3 leaving the reactive site at position 9 available for further reaction with another molecule of substrate. The reasons hydroboration effectively stopped with the trialkylated species when six cage vertices remained unsubstituted were not completely clear. That the scrambling of the vertices was still occurring in the trialkyl species was shown by the identification of a dioctylhexyl species from the competiton reaction between trihexylthiaborane and 1-octene. One must conclude that the 1, 3 and 9 positions on the cage are sterically favored to the extent that rearrangement of the cage to put an alkyl group on one of the remaining positions energetically competes with a cage closure isomerization which begins to become significant when temperatures rise above 200 C.

No aspects of the reactions of 6-thia-nido-decaborane(11) with alkynes were noted that are at variance with the the results found with alkenes. Despite the bulky nature of the thiaborane moiety, two cages could be attached to the same carbon atom by successive reaction steps with a triple bond provided, however, that the triple bond was in a terminal position on the chain. This rould not be achieved when the triple bond was in the center of a chain. Because of the electrophilic nature of the boron cage, it is likely that the alkene produced as the first hydroboration product of an alkyne has an enhanced electron density at the alpha carbon atom. This provides increased susceptibility to attack by a second thiaborane unit. When the double bond is in the interior of a

chain, however, steric factors become sufficiently important to prevent further reaction.

The reversible nature of the hydroboration reaction with olefins together with the ability of the cage to react with more than one double bond suggests a potentially useful application of thiaborane as a cross linking agent for unsaturated polymers. Curing could be carried out at elevated temperatures to give a thermoset plastic but one which, because of the reversible nature of the process, might also possess thermoplastic properties. This idea was not pursued experimentally beyond demonstrating that polybutadiene could be cross linked by 6-SB H without fragmenting the parent polymer.

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